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## [ $\mu-N, N^{\prime}$-Bis(3-aminopropyl)oxamidato(2-)]-bis[(2,2'-bipyridine)copper(II)] dinitrate

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## Key indicators

Single-crystal X-ray study
$T=203 \mathrm{~K}$
Mean $\sigma(\mathrm{C}-\mathrm{C})=0.003 \AA$
$R$ factor $=0.026$
$w R$ factor $=0.072$
Data-to-parameter ratio $=15.5$
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

[^0]The title compound, $\left[\mathrm{Cu}_{2}\left(\mathrm{C}_{8} \mathrm{H}_{16} \mathrm{~N}_{4} \mathrm{O}_{2}\right)\left(\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{~N}_{2}\right)_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}$, contains a centrosymmetric binuclear copper(II) complex bridged by a deprotonated oxamide ligand. The Cu atoms have a distorted square-pyramidal coordination geometry, with one of the $2,2^{\prime}$-bipyridine N atoms at the apex. The copper complex cations assemble in chains along the $c$ axis via $\pi-\pi$ overlaps of bipyridine ligands of neighbouring complexes. These chains are connected in the crystal structure via N $\mathrm{H} \cdots \mathrm{O}$ and $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds with the nitrate ions.

## Comment

The oxamidate dianion is a versatile bridging ligand used in the design and synthesis of polymetallic complexes (Ojima \& Nonoyama, 1988; Ruiz et al., 1999). A large variety of homoand heterobinuclear complexes of multidentate ligands based on functionalized oxamides have been reported. The title complex, (I), was prepared by Ojima \& Nonoyama (1972) from a reaction of $N, N^{\prime}$-bis(3-aminopropyl)oxamidatocopper(II), Cu (apoxd), with mono( $2,2^{\prime}$-bipyridine)copper(II) nitrate, $[\mathrm{Cu}($ bipy $)]\left(\mathrm{NO}_{3}\right)_{2}$, in alkaline solution, and was characterized by magnetic and spectroscopic measurements.


The molecular structure of (I), $\left[\mathrm{Cu}_{2}(\right.$ apoxd $\left.)(\text { bipy })_{2}\right]\left(\mathrm{NO}_{3}\right)_{2}$, is shown in Fig. 1. The complex cation, $\left[\mathrm{Cu}_{2}\right.$ (apoxd)(bipy) $\left.)_{2}\right]^{2+}$, is a centrosymmetric dimer. Two five-coordinate $\mathrm{Cu}^{\mathrm{II}}$ ions are bridged by the deprotonated oxamide group of the $N, N^{\prime}$-bis(3-aminopropyl)oxamide ligand in a trans conformation, with $\mathrm{Cu} \cdots \mathrm{Cu}=5.2504$ (4) $\AA$. Each five-coordinate $\mathrm{Cu}^{\text {II }}$ ion has a near square-pyramidal geometry, with a longer contact to atom O2 [3.115 (3) Å] of the nitrate anion from beneath the basal plane of the coordination pyramid (Table 1). Atoms N 2 and O 1 of the bridging oxamidate anion occupy adjacent positions on the base of the pyramid along with atoms N1 and N3. Atom N4 of the 2, 2'-bipyridine ligand is at the apex of the pyramid, with the $\mathrm{Cu}-\mathrm{N} 4$ distance significantly longer than the basal $\mathrm{Cu}-\mathrm{N} 3$ distance, indicative


Figure 1
The molecular structure of (I), showing the atom-numbering scheme, with $50 \%$ probability displacement ellipsoids. H atoms are shown as arbitrary spheres. The dashed line indicates a hydrogen bond. (Symmetry code for unlabelled atoms: $-x, 1-y,-z$.)


Figure 2
The packing arrangement of complex (I), viewed along the $a$ axis, showing the $\pi-\pi$ stacking between complex cations. H atoms have been omitted.
of a Jahn-Teller distorted geometry. The 12-atom plane of the 2,2'-bipyridine ligand (C5-C14/N3/N4, r.m.s. deviation $0.05 \AA$ ) makes an angle of $88.10(4)^{\circ}$ to the $\mathrm{Cu} / \mathrm{O} 1 / \mathrm{N} 1 / \mathrm{N} 2 / \mathrm{N} 3$ basal plane (r.m.s. deviation $0.252 \AA$ ). The overall molecular geometry of the $\left.\left[\mathrm{Cu}_{2} \text { (apoxd)(bipy) }\right)_{2}\right]^{2+}$ cation is very similar to an analogous $\left.\left[\mathrm{Cu}_{2} \text { (apoxd)(pyrimidine) }\right)_{2}\right]^{2+}$ complex cation (Dominguez-Vera et al., 1998) and a related $\left[\mathrm{Cu}_{2}(\text { aeoxd })(\text { diazafluorenone })_{2}\right]^{2+}$ complex (Li et al., 2005).

The ions of (I) assemble in the crystal structure as shown in Fig. 2. The dimeric units form chains along the $c$ axis via $\pi-\pi$ stacking of the $2,2^{\prime}$-bipyridine ligands with those of adjacent complexes (interplanar distance $3.459 \AA$ ). The O atoms of the nitrate ion form hydrogen bonds to H atoms on the primary amine atom N 1 , the methylene C atoms C 1 and C 3 , and bipyridine C atoms C 7 and C8 (Table 2). These connect each of the $\left[\mathrm{Cu}_{2}(\text { apoxd })(\text { bipy })_{2}\right]^{2+}$ cation chains within the crystal structure.

## Experimental

Complex (I) was prepared and crystallized as described by Ojima \& Nonoyama (1972).

## Crystal data

$\left[\mathrm{Cu}_{2}\left(\mathrm{C}_{8} \mathrm{H}_{16} \mathrm{~N}_{4} \mathrm{O}_{2}\right)\left(\mathrm{C}_{10} \mathrm{H}_{8} \mathrm{~N}_{2}\right)_{2}\right]-$

$$
\left(\mathrm{NO}_{3}\right)_{2}
$$

$M_{r}=763.72$
Triclinic, $P \overline{1}$
$a=8.9069$ (3) $\AA$ 。
$b=10.3003$ (4) $\AA$
$c=10.3457$ (4) $\AA$
$\alpha=103.290(1)^{\circ}$
$\beta=107.605(1)^{\circ}$

$$
\begin{aligned}
& \gamma=112.436(1)^{\circ} \\
& V=769.31(5) \AA^{3} \\
& Z=1 \\
& D_{x}=1.648 \mathrm{Mg} \mathrm{~m}^{-3} \\
& \text { Mo } K \alpha \text { radiation }^{\mu=1.45 \mathrm{~mm}^{-1}} \\
& T=203(2) \mathrm{K} \\
& \text { Prism, green } \\
& 0.20 \times 0.18 \times 0.15 \mathrm{~mm}
\end{aligned}
$$

## Data collection

Siemens SMART CCD area-
detector diffractometer
$\omega$ scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)
$T_{\text {min }}=0.760, T_{\text {max }}=0.812$
7305 measured reflections
3353 independent reflections
3123 reflections with $I>2 \sigma(I)$
$R_{\text {int }}=0.015$
$\theta_{\text {max }}=27.5^{\circ}$

## Refinement

Refinement on $F^{2}$
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.026$
$w R\left(F^{2}\right)=0.072$
$S=1.06$
3353 reflections
217 parameters
H -atom parameters constrained

$$
\begin{gathered}
w=1 /\left[\sigma^{2}\left(F_{\mathrm{o}}^{2}\right)+(0.0412 P)^{2}\right. \\
\quad+0.358 P] \\
\text { where } P=\left(F_{\mathrm{o}}^{2}+2 F_{\mathrm{c}}^{2}\right) / 3 \\
(\Delta / \sigma)_{\max }<0.001 \\
\Delta \rho_{\max }=0.62 \mathrm{e}^{-3} \AA^{-3} \\
\Delta \rho_{\min }=-0.50 \mathrm{e}^{-3}
\end{gathered}
$$

Table 1
Selected geometric parameters ( $\left(\AA,{ }^{\circ}\right)$.

| $\mathrm{Cu}-\mathrm{N} 2$ | $1.9468(13)$ | $\mathrm{Cu}-\mathrm{N} 3$ | $2.0173(14)$ |
| :--- | ---: | :--- | ---: |
| $\mathrm{Cu}-\mathrm{O} 1^{\mathrm{i}}$ | $2.0126(12)$ | $\mathrm{Cu}-\mathrm{N} 4$ | $2.2276(15)$ |
| $\mathrm{Cu}-\mathrm{N} 1$ | $2.0166(14)$ |  |  |
| $\mathrm{N} 2-\mathrm{Cu}-\mathrm{O} 1^{\mathrm{i}}$ | $83.86(5)$ | $\mathrm{N} 1-\mathrm{Cu}-\mathrm{N} 3$ | $91.03(6)$ |
| $\mathrm{N} 2-\mathrm{Cu}-\mathrm{N} 1$ | $92.71(6)$ | $\mathrm{O} 1^{i}-\mathrm{Cu}-\mathrm{N} 4$ | $104.96(5)$ |
| $\mathrm{O} 1^{\mathrm{i}}-\mathrm{Cu}-\mathrm{N} 1$ | $149.59(6)$ | $\mathrm{N} 1-\mathrm{Cu}-\mathrm{N} 4$ | $105.21(6)$ |
| $\mathrm{N} 2-\mathrm{Cu}-\mathrm{N} 3$ | $175.79(5)$ | $\mathrm{N} 3-\mathrm{Cu}-\mathrm{N} 4$ | $77.33(6)$ |
| $\mathrm{O} 1^{\mathrm{i}}-\mathrm{Cu}-\mathrm{N} 3$ | $91.94(5)$ |  |  |
| Symmetry |  |  |  |

Table 2
Hydrogen-bond geometry ( $\AA,{ }^{\circ}$ ).

| $D-\mathrm{H} \cdots A$ | $D-\mathrm{H}$ | $\mathrm{H} \cdots A$ | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{N} 1-\mathrm{H} 1 A \cdots \mathrm{O} 2$ | 0.91 | 2.21 | 2.928 (2) | 135 |
| $\mathrm{N} 1-\mathrm{H} 1 A \cdots \mathrm{O} 2{ }^{\text {ii }}$ | 0.91 | 2.63 | 3.080 (2) | 111 |
| $\mathrm{N} 1-\mathrm{H} 1 \mathrm{D} \cdots \mathrm{O} 4^{\text {ii }}$ | 0.91 | 2.16 | 3.032 (2) | 161 |
| $\mathrm{C} 1-\mathrm{H} 1 \mathrm{~B} \cdots \mathrm{O} 4^{\text {iii }}$ | 0.98 | 2.53 | 3.413 (3) | 150 |
| $\mathrm{C} 3-\mathrm{H} 3 \mathrm{~B} \cdots \mathrm{O} 4^{\text {iii }}$ | 0.98 | 2.68 | 3.528 (2) | 145 |
| $\mathrm{C} 7-\mathrm{H} 7 A \cdots \mathrm{O} 4{ }^{\text {iv }}$ | 0.94 | 2.45 | 3.348 (2) | 160 |
| $\mathrm{C} 8-\mathrm{H} 8 A \cdots 3^{\text {iv }}$ | 0.94 | 2.65 | 3.253 (3) | 122 |

Symmetry codes: (ii) $-x,-y+1,-z+1$; (iii) $x+1, y, z$; (iv) $x, y-1, z$.

H atoms were placed in calculated positions and refined using a riding model, with $\mathrm{C}-\mathrm{H}=0.93-0.98 \AA$ and $\mathrm{N}-\mathrm{H}=0.91 \AA$, and with $U_{\text {iso }}(\mathrm{H})=1.2 U_{\text {eq }}(\mathrm{C}, \mathrm{N})$ for methylene and amine H atoms, or $1.5 U_{\mathrm{eq}}(\mathrm{C})$ for aromatic C atoms in the bipyridine group.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and MERCURY (Macrae et

## metal-organic papers

al., 2006); software used to prepare material for publication: WinGX (Farrugia, 1999).

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## References

Dominguez-Vera, J. M., Moreno, J. M., Galvez, N., Suarez-Varela, J., Colacio, E., Kivekas, R. \& Klinga, M. (1998). Inorg. Chim. Acta, 281, 95-100.

Farrugia, L. J. (1997). J. Appl. Cryst. 30, 565.
Farrugia, L. J. (1999). J. Appl. Cryst. 32, 837-838

Li, Y.-P., Yang, P., Huang, Z.-X. \& Xie, F.-X. (2005). Acta Cryst. C61, m7-m9. Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. \& van de Streek, J. (2006). J. Appl. Cryst. 39, 453-457.

Ojima, H. \& Nonoyama, K. (1972). Z. Anorg. Allg. Chem. 389, 75-82.
Ojima, H. \& Nonoyama, K. (1988). Coord. Chem. Rev. 92, 85-111.
Ruiz, R., Faus, J., Lloret, F., Julve, M. \& Journaux, Y. (1999). Coord. Chem. Rev. 193-195, 1069-1117.
Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (1997). SHELXS97 and SHELXL97 (Release 97-1). University of Göttingen, Germany.
Siemens (1995). SHELXTL (Version 5.03), SMART (Version 4.050) and SAINT (Version 4.050). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.


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